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# Force Field Parameters for Carbohydrates

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## ABSTRACT

A new set of force field parameters for carbohydrates is reported. The parameter set is based on the CHARMM22 force field of Karplus and co-workers. The parameterization is based on newly performed high-level *ab initio* calculations [MP2/6-311 + G(2d,2p)/6-31G\*\*] of fragment molecules. A good agreement of the modified force field and *ab initio* data is achieved, which is demonstrated with a variety of molecules. © 1996 by John Wiley & Sons, Inc.

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## Introduction

In today's computational chemistry, several methods exist to calculate the energetical properties of an arrangement of atoms. The most frequently used methods are based on quantum chemistry (*ab initio* and semiempirical) and force field calculations.

The *ab initio* technique offers, in principle, the possibility to obtain observables of every system without any predetermined parameters. In the practical implementation, the observables can only be approximated on the basis of a given set of basis functions, with a rise in computational expense of  $N^x \geq 2.7$ , where  $N$  is the number of basis functions. At present, exact *ab initio* calculations

are only possible for relatively small molecular systems.

In semiempirical methods the number of treatable atoms can be increased by introducing empirical parameters. In principle, the unlimited applicability of the *ab initio* technique is lost for a gain in practical applicability (i.e., the size of a treatable system is increased in semiempirical treatments), but the validity of this method must be carefully checked.

In force field calculations the number of atoms can be chosen to be substantially larger than in the molecular orbital (MO) treatments just described. Using a force field, the interactions of atoms (or, more generally, particles) are described by an analytical function, which must be parameterized for every class of systems. Most of the current force fields were developed for proteins but have been extended to treat various kinds of other molecules.

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The goal of this work was to modify an existing force field for the demands of carbohydrates. The basis of the parameterization is the new CHARMM22 force field of Karplus and co-workers<sup>1,2</sup> for proteins, nucleic acids, and lipids. In this force field, much attention was paid to generating effective parameters for the simulation of solvated biological molecules.

It was the aim of this work to generate force field parameters for carbohydrates for simulations of these and with other molecules. Consequently, the new force field parameters had to be consistent with parameters for other molecules. Furthermore, the present study is intended to be the basis for future simulations of big systems of carbohydrates in crystal and different solvents, wherein speed and elaborate manipulation of the system, as possible with Charmm, are needed.

An empirical force field like CHARMM22 can be subdivided into three distinct parts: intermolecular interactions, vibrational modes, and torsional flexibility. These parts of the CHARMM22 force field can be seen in the functional form

$$\begin{aligned}
 V = & \sum_{\text{bonds}} k_b(r - r_0)^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_0)^2 \\
 & + \sum_{\text{impropers}} k_l(l - l_0)^2 \\
 & + \sum_{j>i} \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) \\
 & + \sum_{\text{torsions}} k_\phi[1 + \cos(n\phi - \delta)] \quad (1)
 \end{aligned}$$

where the following abbreviations are used:

$r$ : bond length  
 $k_b$ : force constant (bond)  
 $\theta$ : bending angle  
 $k_\theta$ : force constant (bending)  
 $\phi$ : torsional angle  
 $\delta$ : phase angle  
 $\iota$ : improper torsional angle  
 $\iota_0$ : equilibrium improper torsional angle  
 $r_{ij}$ : distance

nates (bond lengths, valence angles, and out-of-plane displacements). These terms essentially represent the vibrational frequencies as experimentally observed. The intermolecular interactions are treated by Coulombic and Lennard-Jones (12, 6) pairwise interactions. These interactions are essential for the interaction of the carbohydrates with their solvent and for the heat of solvation. The third and last contributions are the potentials associated with the dihedral angles, representing most of the molecular flexibility. In some investigations the authors do not separate these terms from the vibrational part, but they define the flexibility and relative order of the conformations of flexible molecules and not primarily the vibrational frequencies.

In most empirical force fields used for the simulation of biological systems, the nonbonded parameters (Lennard-Jones and charge distribution) are derived on the basis of intensive quantum chemical analysis of intermolecular interactions between small fragment molecules (e.g., methanol) and water. In addition, the parameters are calibrated to the free energy of solvation. It is generally accepted that the nonbonded parameters will not vary significantly if these fragments are put together to model a larger molecule. Also, the intramolecular parameters concerning the bond stretches and valence angle vibrations are essentially local and will not change as the fragments increase. Therefore, all these parameters can be derived from the study of small compounds and by experiments.

The situation is different for the dihedral poten-

$r_0$ : equilibrium bond length  
 $\theta_0$ : equilibrium bending angle  
 $n$ : multiplicity  
 $k_\phi$ : force constant (torsion)  
 $k_\phi$ : force constant (improper torsion)  
 $A_{ij}, B_{ij}$ : Lennard-Jones parameters  
 $q_i, q_j$ : charges

The vibrational part of the force field is represented by harmonic potentials for internal coordi-

nates. In many empirical force fields, these are defined only by considering the type of the two

central atoms, because if the terminal atom types are also used, the number of possible combinations would lead to a drastic increase in the number of torsions and hence in the number of torsional parameters to be determined. Furthermore, it is not easy to derive these parameters from experiments, because

1. The vibrational frequencies associated with torsional modes are very low and can hardly be measured.
2. The focus of interest for the description of a torsional degree of freedom is not put on the vibrational modes around the minima of such a degree of freedom, but in the energetical differences between minima and in the energy of the transition states between them.

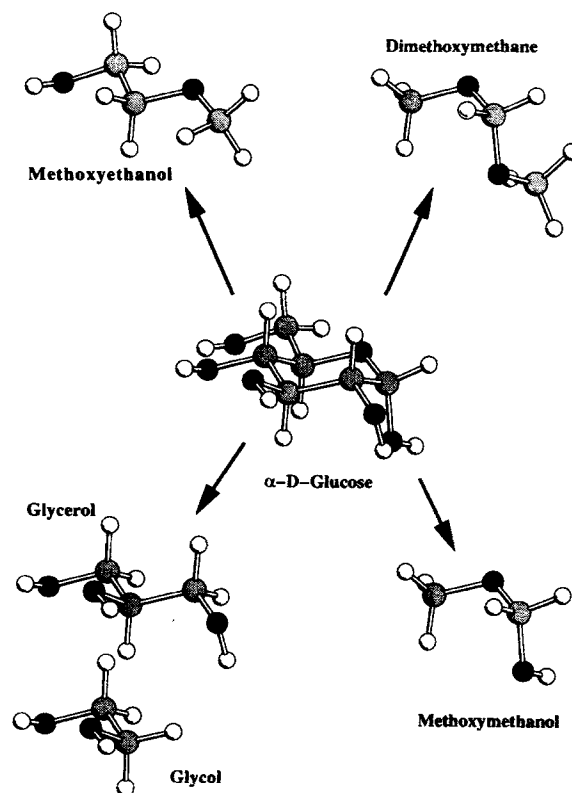
Therefore, the only possibility to determine these parameters is to perform theoretical calculations on the molecular energetics. Because there is no way to cross-validate the theoretical calculations with experimental (spectroscopic) data, the quality of the calculations must be very high, leading in most cases to great computational expense. The need for reliable torsional force field parameters is emphasized by the consideration that conformational changes in biomolecules are always changes of torsional degrees of freedom. For the special case of carbohydrates, torsional degrees of freedom are often coupled to effects like changes in polarization or orbital-orbital interactions, such as the gauche effect<sup>3</sup> or the anomeric effect,<sup>4-6</sup> although it was found that for carbohydrates-like molecules the influence of bond polarization is not important for molecular mechanics.<sup>7</sup> The torsional parameters are thus needed to model the energetics of these effects in a classical force field, without polarization terms and constant atomic charges. The focus of this work is on the torsional parameters, which seem to be the least reliable part of a force field. This has also been shown in a comparison between force fields for the case of the four conformers of glycol<sup>8</sup> lowest in energy.

In the CHARMM22 force field, the partial charges were derived to treat the polarization effects arising from the solvent in an effective manner and to reproduce the experimentally measured free energies of solvation. The harmonic force constants and equilibrium distances and angles were fitted to the experimentally observed vibrational frequencies. These local parameters should not

change when larger molecules are composed, as there are no known electron delocalization effects for these compounds. With the exception of minor changes in the Lennard-Jones terms of the oxygens, these parameters were not changed by the present parameterization. As described earlier, the new torsional parameters are based on accurate *ab initio* calculations of small molecules representing fragments of carbohydrates, namely 1,2-ethanediol (glycol), 1,2,3-propanetriol (glycerol), 2-methoxyethanol, methoxymethanol, and dimethoxymethane. These fragments contain all combinations of dihedral atom types in nonsubstituted carbohydrates (see Fig. 1).

Quantum chemical calculations were performed with these fragments to obtain relative energies of conformers and barrier heights. The obtained data was used to modify the force field for the best possible agreement. In doing so, the focus of the parameterization was on the conformers of lowest energy, because these are the conformations which play the most important role in simulations.

In the original CHARMM22 force field, the torsional degrees of freedom were represented by a



**FIGURE 1.** Fragmentation of a carbohydrate ( $\alpha$ -D-glucose) in small molecules for the parameterization of a force field.

cosine term with a multiplicity of three. This term only describes the height of the barrier between the three possible conformers (torsional angle =  $60^\circ$ ,  $-60^\circ$ , and  $180^\circ$ ) and not the energy difference between the conformers. In the present parameterization, a onefold cosine term was additionally introduced for most of the torsions, which allows the modeling of the differences in energy between the conformers.

The level of theory of the *ab initio* calculations was determined in a preliminary study.<sup>9</sup> It was found, as in the work of Cramer and Truhlar,<sup>10</sup> that due to the importance of intramolecular non-bonded interactions (especially H bonds), the widely used HF/6-31G\*\*/F/6-31G\*\* calculations are not adequate. As a consequence, all molecules were calculated using HF/6-31G\*\* for the determination of the geometries. With these geometries, the relative energies of the conformers were calculated using a 6-311 + G(2d,2p) basis set and Møller-Plesset second-order perturbation theory (MP2) for the partial inclusion of electron-electron correlation. For all molecules except glycerol, all possible conformers were calculated. In the case of glycerol, 16 conformers were calculated. Furthermore, for glycol and methoxyethanol selected transition states of interest for the parameterization were calculated. This work is also intended to serve as a database of *ab initio* data for other applications. Therefore, not only are tables with the relative energies of the conformers presented, but also additional tables with the complete *ab initio* geometries (see the Appendix).

## Computational Details

All *ab initio* calculations were performed using Gaussian90<sup>11</sup> on a Cray YMP at the KFA Jülich and an SNI S400/40 at the HRZ Darmstadt. The *ab initio* geometries were all optimized at the HF/6-31G\*\*<sup>12</sup> level of theory. On the basis of these geometries, single-point calculations were performed using the MP2/6-311 + G(2d,2p) level of theory. The starting points of the geometry optimizations were in most cases, published HF/4-21G optimized geometries. The geometries of transition points were derived using the "TS" facility available in Gaussian90, which enables one to find a maximum in energy along one degree of freedom while relaxing all other degrees of freedom to a minimum. As for the conformers, the energies of

the transition states were calculated on an MP2/6-311 + G(2d,2p) basis.

The force field calculations were performed using the CHARMM22<sup>1,2</sup> package on an SGI Indigo workstation. In all geometry optimizations, all degrees of freedom were relaxed. Only for the determination of a transition state, the torsional angle was restrained by a harmonic potential. The positional root mean square (rms) deviations were determined by a best rigid-body molecular fit routine.<sup>13</sup> All atoms of a molecule were included in this fit. The naming of the conformers is defined by the setting of the essential dihedral angles.<sup>14</sup> All molecule plots were generated using the MOLCAD<sup>15</sup> program package developed in the group of the authors.

## Calculations

### 1,2-ETHANEDIOL (GLYCOL)

Knowledge of the relative energies of the conformers of glycol and the transition states leading

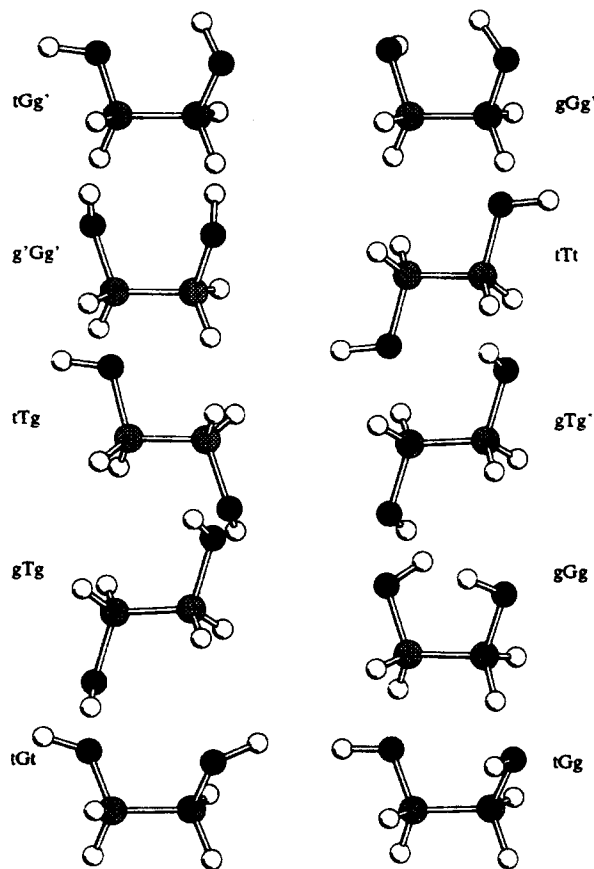


FIGURE 2. The conformers of glycol.

from one conformer to another allows the parameterization of the central H—O—C—C—O—H torsion, which is present in most carbohydrates. In Figure 2 all 10 possible conformers of glycol are depicted. In a preliminary study,<sup>9</sup> glycol was used to determine the level of theory used for the *ab initio* calculations in the present study. Tables with the complete geometries of the conformers were also published. In Table I the relative energies calculated using MP2/6-311 + G(2d, 2p) are listed. In Figure 3 the calculated transition states are depicted, and tables with the numerical values of the geometries can be found in the Appendix. The corresponding relative energies are listed in Table II. The origin of the energy scale in Tables I and II is the energy of the most stable conformer of glycol (tGg'). In Figure 4 the pathways described by the calculated transition states are depicted. The transition states were chosen to connect the conformers lowest in energy. In Figure 5 the naming convention of the atoms in glycol is illustrated. In Table III the atoms of glycol are listed together with the assigned atom types and partial charges. The results after the modification of CHARMM22 are compared to the *ab initio* data in Tables I and II. The geometry of the transition states was derived by increasing the concerned torsional angle in steps of 10 degrees, starting with an angle of 20 degrees up to 160 degrees. The torsional angle was restrained by a harmonic potential, and the rest of the geometry was kept flexible. At each step, an energy minimization was performed.

In Table II the highest relative energy is given

together with the torsional angle. The origin of the energy scale is always the lowest-energy conformer (tGg'). For glycol, the effect of the modifications on the force field is shown. The energies calculated with the original force field are listed in Tables I and II as well.

Before the modification of the force field, the energetical order of the conformers of glycol, as calculated by CHARMM, is incorrect. The conformer tTt is calculated as the global minimum, in contradiction to the *ab initio* calculations and experiment.<sup>16,17</sup>

After the modification, the energetical order of the conformers is correctly represented. The cen-

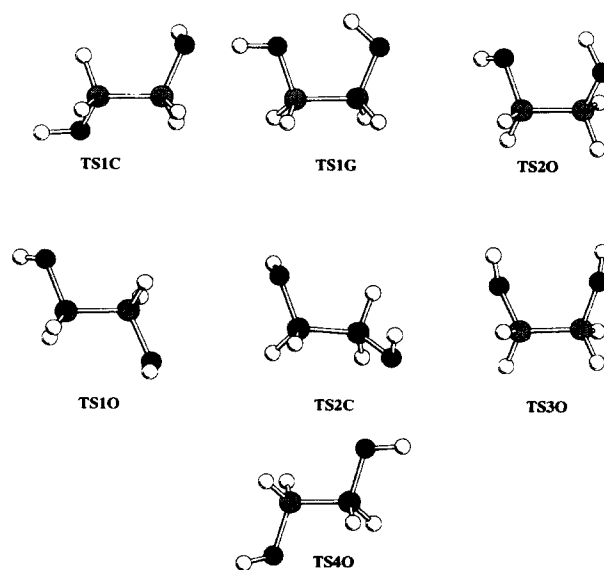


FIGURE 3. Calculated transition states.

**TABLE I.**  
Relative Energies (kcal / mol) of the Glycol Conformers, Calculated Using MP2 / 6-311 + G(2d, 2p) // HF / 6-31G\*\*, Together with the Results of the Force Field.

	6-311+G(2d,2p)		Charmm22 original	Charmm22 modified	
	HF	MP2	Energy	Energy	RMS
tGg'	0.00	0.00	0.72	0.00	0.074
gGg'	0.69	0.50	1.16	0.36	0.089
g'Gg'	1.03	1.06	1.58	0.92	0.041
tTt	1.69	2.63	0.00	2.62	0.050
tTg	2.08	2.83	0.96	3.59	0.065
gTg'	2.28	2.86	0.75	3.39	0.058
gTg	2.59	3.09	2.10	4.75	0.077
gGg	3.04	3.29	→gGg'	→gGg'	
tGt	2.90	3.24	→g'Gg'	→g'Gg'	
tGg	3.46	3.78	→tTg	→tTg	

Arrows indicate transitions of conformers into others.

**TABLE II.**  
Relative Energies (kcal / mol) of Some Selected Transition States of Glycol, Calculated Using MP2 / 6-311 + G(2d, 2p) // HF / 6-31G\*\*, Together with the Results of the Force Field.

	Affected Torsion	6-311+G(2d,2p)			Charmm22 original	Charmm22 modified	
		HF	MP2	Tor. Angle	Energy	Energy	Tor. Angle
TS1C	O1-C1-C2-O2	5.36	5.74	124.41	6.55	7.99	130
TS1G	O1-C1-C2-O2 HO1-O1-C1-C2	6.92	6.95	0.00 0.00	17.93	15.72	0.0
TS1O	HO1-O1-C1-C2	2.73	3.37	122.10	2.60	5.24	110
TS2C	O1-C1-C2-O2	6.07	6.34	121.65	5.04	6.13	120
TS2O	HO1-O1-C1-C2	1.26	1.22	124.11	1.82	1.05	120
TS3O	HO1-O1-C1-C2	2.61	1.62	88.4	1.82	1.05	120
TS4O	HO1-O1-C1-C2	2.48	3.29	121.10	1.15	3.77	110

Torsional angles are given in degrees.

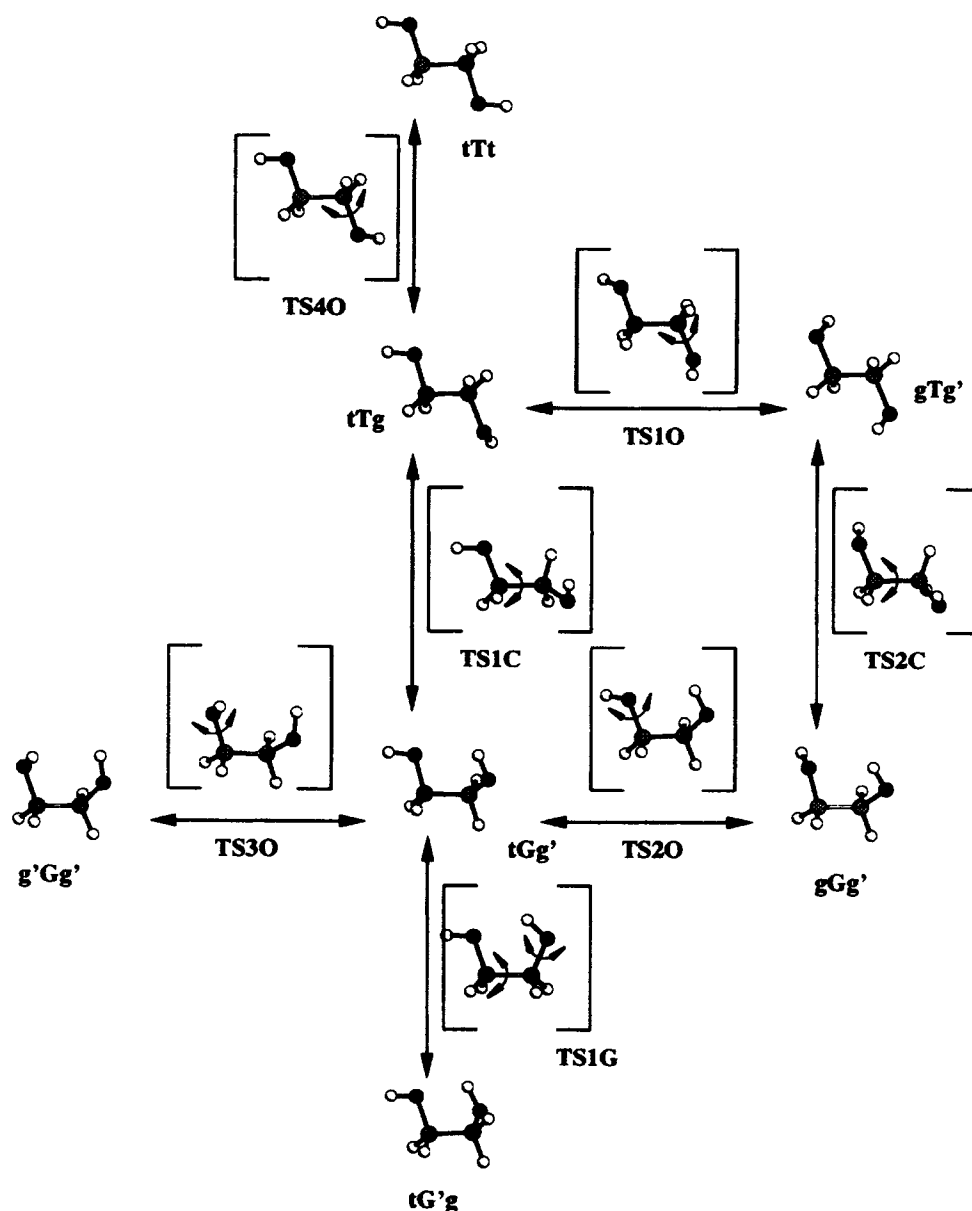


FIGURE 4. Pathways between conformers covered by the calculated transition states.

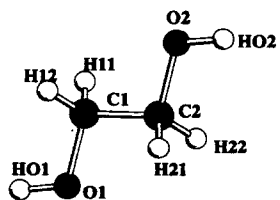


FIGURE 5. Naming convention of the atoms in glycol.

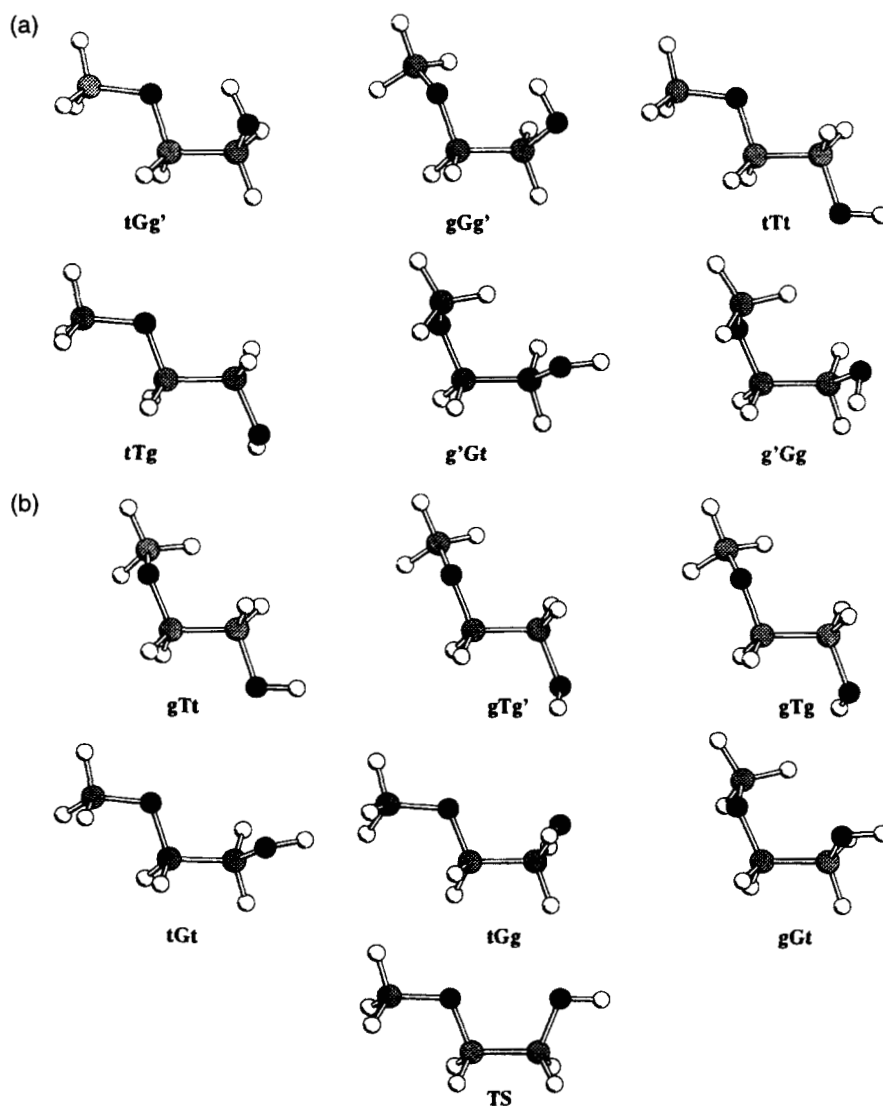
TABLE III.  
Assignment of Atom Types and Partial Charges  
to the Atoms of Glycol.

Atom	Atom type	Charge	Atom	Atom type	Charge
C1	CN6	0.05	C2	CN6	0.05
H11	HN6	0.09	H21	HN6	0.09
H12	HN6	0.09	H22	HN6	0.09
O1	ON5	-0.66	O2	ON5	-0.66
HO1	HN5	0.43	HO2	HN5	0.43

tral goal of this work is to establish the best agreement between force field and *ab initio* results for the lowest-energy conformers. The energetical differences are smaller than 0.76 kcal/mol, and the positional rms values are smaller than 0.089 Å. However, the force field is not able to reproduce all conformers that are found to be stable by the *ab initio* technique. The three conformers highest in energy are unstable when a geometry optimization in vacuum with the force field is performed. One of these unstable conformers, tGg, however, was found to be stable and important in aqueous solution.<sup>18,19</sup> But if the results of the force field are

compared with the results of semiempirical calculations published in ref. 9, the results of the force field are superior to the semiempirical results. Furthermore, the missing conformers are the highest-energy conformers in vacuum. If a Boltzmann distribution of the conformers is assumed, the missing conformers represent only 0.6% of the conformers at 300 K. The (stabilizing) effect of a solvent was not included in the calculations presented here.

The limitations of a classical force field become more evident when the results between *ab initio* and force field are compared for the transition



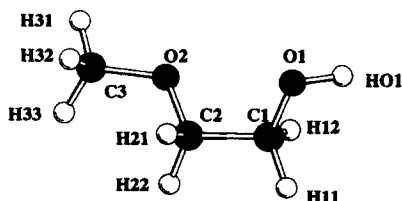
**FIGURE 6.** (a) The conformers of 2-methoxyethanol. (b) The conformers of 2-methoxyethanol plus calculated transition state TS.

states (Table II). The differences are greatest for the TS1G transition state, due to the nonbonded repulsion of the planar atoms.

## 2-METHOXYETHANOL

As can be seen in Figure 1, 2-methoxyethanol represents the exocyclic  $O_5-C_5-C_6-O_6$  torsion of  $\alpha$ -D-glucose, a type of torsion which is present in most natural carbohydrates. The conformational changes of this torsional degree of freedom have been found to be important (e.g., for the explanation of the physical properties of cellulose I and cellulose II crystals). In previous studies on the conformation of  $\alpha$ -D-glucose in aqueous solution, it was not always possible to represent the conformational behavior around this torsion<sup>20</sup> when compared to experimental data.<sup>21</sup> Therefore, the correct representation of the energetics around this torsion was one of the main items of this parameterization. The 4-21G derived geometries by Vazquez et al.<sup>22</sup> provided the starting point for the geometry optimization of 2-methoxyethanol. The geometries of all 12 possible conformers were calculated using HF/6-31G\*\*. The conformers are shown in Figure 6, and tables with the numerical values of the geometries can be found in the Appendix. The relative energy of one transition state, corresponding to the transition state TS1G of glycol five atoms in a planar arrangement), was also calculated. The transition state is included in Figure 6. The naming convention of the atoms in 2-methoxyethanol is shown in Figure 7, and the assignment of atom types and partial charges is shown in Table IV. The relative energies of the conformers and the transition state are listed in Table V, together with the results of the modified force field.

For 2-methoxyethanol, the same good agreement as found for glycol between force field and *ab initio* results could be achieved. Not all conformers can be represented by the force field, but



**FIGURE 7.** Naming convention for the atoms in 2-methoxyethanol.

**TABLE IV.**  
Assignment of Atom Types and Partial Charges to the Atoms of Methoxyethanol.

Atom	Atom type	Charge	Atom	Atom type	Charge
C1	CN6	0.03	H22	HN6	0.08
H11	HN6	0.08	O2	ON6	-0.30
H12	HN6	0.08	C3	CN6	-0.06
O1	ON5	-0.66	H31	HN6	0.07
HO1	HN5	0.43	H32	HN6	0.07
C2	CN6	0.03	H33	HN6	0.07
H21	HN6	0.08			

**TABLE V.**  
Relative Energies (kcal / mol) of the Methoxyethanol Conformers, Calculated Using MP2 / 6-311 + G(2d, 2p) // HF / 6-31G\*\*, Together with the Results of the New Force Field.

	6-311+G(2d,2p)		Charmm22	
	HF	MP2	Energy	RMS
tGg'	0.00	0.00	0.00	0.065
gGg'	2.18	1.71	1.43	0.170
tTt	1.72	2.72	2.71	0.058
tTg	2.06	2.86	3.57	0.064
g'Gt	3.57	3.44	4.51	0.262
g'Gg	4.31	4.04	5.84	0.323
gTt	3.66	4.28	→tTt	
gTg'	3.87	4.30	4.57	0.176
gTg	4.17	4.55	→tTg	
tGt	2.83	3.20	→tGg'	
tGg	3.29	3.59	→tGg'	
gGt	4.85	4.78	→gGg'	
TS	11.64	12.04	11.96	

Arrows indicate transitions of conformers into others.

the important fact is that the conformers lowest in energy are represented. For these conformers, the agreement of the relative energies is better than 1.8 kcal/mol (if the conformer g'Gg' is omitted, the agreement is even better than 0.9 kcal/mol), the positional rms is smaller than 0.323 Å, and throughout the parameterization a better agreement was achieved. The energy of the transition state can be represented within 0.8 kcal/mol.

## 1,2,3-PROPANETRIOL (GLYCEROL)

Glycerol contains the same atom types as glycol, but offers the possibility to parameterize the balance of the O—C—C—O and the O—C—C—C torsion. For glycerol, not all possible conformers were calculated. The geometries published by van den Enden<sup>23</sup> and van Alsenoy<sup>24</sup> were the starting



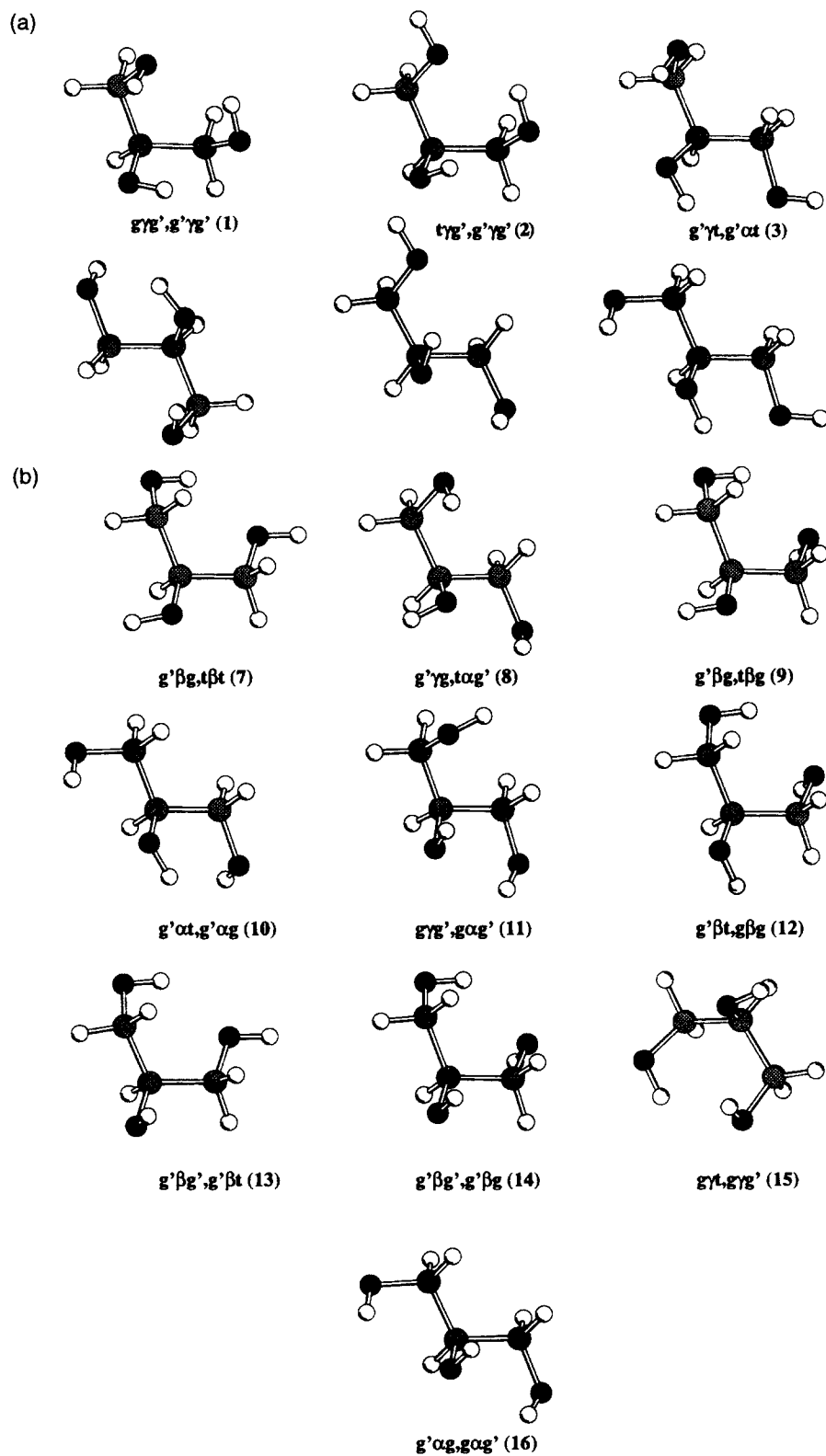


FIGURE 8. The calculated conformers of glycerol. In brackets the numbering used in this work.

points. Sixteen conformers were calculated and are depicted in Figure 8. The naming of the conformers is taken from ref. 23.

The relative energies of these conformers are listed in Table VI. For glycerol, in the course  $4-21G \rightarrow 6-31G^{**} \rightarrow 6-311 + G(2d, 2p)$ , a number of changes appeared in the energetical order of the conformers. In Table VI only the final result is shown.

In Figure 9 the naming convention of the atoms in glycerol is illustrated, and in Table VII atom types and atomic charges are assigned to these atoms. In Table VI the results of the force field after the modification are compared to the *ab initio* results. Again, relative energies and positional rms values are shown. In the comparison of force field and *ab initio* techniques, deviations up to 3.8 kcal/mol appear. Out of the 16 conformers, 14 are represented by the force field. One of the missing conformers is a lowest energy, but it was not possible to change the parameters in such a way as to stabilize this conformer.

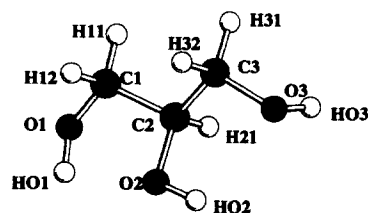
#### METHOXYMETHANOL AND DIMETHOXYMETHANE

Methoxymethanol and dimethoxymethane represent the region around the  $C_1$  atom of  $\alpha$ -D-glucose.

**TABLE VI.**  
Relative Energies (kcal/mol) of the Glycerol Conformers, Calculated Using MP2/6-311 + G(2d, 2p) // HF/6-31G\*\*, Together with the Results of the New Force Field.

	6-311+G(2d,2p)		Charmm22	
	HF	MP2	Energy	RMS
1	0.75	0.00	0.00	0.113
3	0.00	0.26	0.37	0.078
4	0.74	0.75	2.08	0.078
2	1.24	0.85	→1	
6	0.45	1.10	0.66	0.086
5	1.14	1.33	1.51	0.067
10	1.05	1.47	1.42	0.086
8	1.48	1.78	3.29	0.115
11	2.05	2.01	2.88	0.075
16	2.52	2.73	3.02	0.095
7	2.71	3.42	5.28	0.149
15	3.89	3.61	6.92	0.167
9	3.08	3.68	→8	
14	3.95	4.30	7.45	0.137
13	3.85	4.31	7.14	0.154
12	3.79	4.38	8.18	0.139

Arrows indicate transitions of conformers into others.



**FIGURE 9.** Naming convention of the atoms in glycerol.

cose. Methoxymethanol represents the unsubstituted sugar (e.g., in a monomer), and dimethoxymethane represents this region involved in the glycosidic linkage (e.g., in a carbohydrate polymer).

For methoxymethanol, four conformers were calculated and are depicted in Figure 10. For dimethoxymethane, three conformers were calculated and are depicted in Figure 11. The starting points for the calculations were, in the case of dimethoxymethane, the 6-31G\* geometries published by Wiberg and Murck.<sup>5</sup> For methoxymethanol, the starting geometries for the geometry optimization were generated assuming typical values for bond length and bending angles (taken from other fragment molecules), and the torsional angles were set to 60°, -60°, and 180° for + gauche, - gauche and trans positions of the torsions, respectively. The results of the *ab initio* calculation are shown in Tables VIII and IX. In Figure 12 the naming convention of the atoms in dimethoxymethane and methoxymethanol is depicted, and in Tables X and XI atom types and charges are assigned to these atoms. In Tables VIII and IX the results of the modified force field are compared with the *ab initio* results. One out of seven conformers is not represented. For the repre-

**TABLE VII.**  
Assignment of Atom Types and Partial Charges to the Atoms of Glycerol.

Atom	Atom type	Charge	Atom	Atom type	Charge
C1	CN6	0.05	O2	ON5	-0.66
H11	HN6	0.09	HO2	HN5	0.43
H12	HN6	0.09	C3	CN6	0.05
O1	ON5	-0.66	H31	HN6	0.09
HO1	HN5	0.43	H32	HN6	0.09
C2	CN6	0.14	O3	ON5	-0.66
H21	HN6	0.09	HO3	HN5	0.43

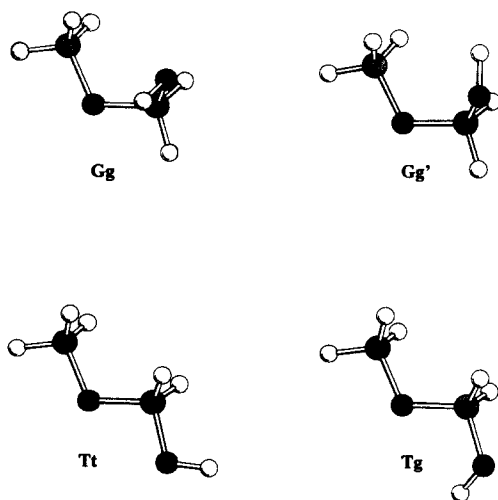


FIGURE 10. The conformers of methoxymethanol.

sented conformers the deviation of energies is better than 0.62 kcal/mol, and the positional rms is smaller than 0.180 Å.

## Conclusion

In this work geometries and energies of molecules, which represent fragments of carbohydrates, were derived using high-level *ab initio* calculations. For most of the molecules, all possible conformers were calculated. A complete list of geometries and relative energies is included. With this data set, the CHARMM22<sup>1,2</sup> force field was modified. In Tables XII to XV the final parameters of the modified force field are listed. A onefold cosine term was introduced to the force field to model the energetics around the torsional degrees of freedom. With values of up to -2.14 kcal/mol, for the force constant of the onefold cosine term, these changes are remarkable and show the impor-

tance of polarization and orbital-orbital interactions for the investigated class of molecules. With the modified force field, the results of the *ab initio* calculations could be represented within 3.8 kcal/mol for the energy and 0.323 Å for the positional rms; for the biggest part of the conformers, the deviation is of the order of one-tenth of a kcal/mol. The force field is not able to represent all conformers that are found to be stable by *ab initio*. However, 34 conformers out of a total of 45 conformers are found to be stable, and the missing conformers are in most cases nonrepresentative high-energy conformers.

TABLE VIII.  
Relative Energies (kcal/mol) of the Dimethoxymethane Conformers, Calculated Using MP2/6-311 + G(2d, 2p) // HF/6-31G\*\*, Together with the Results of the New Force Field.

	6-311+G(2d,2p)		Charmm22	
	HF	MP2	Energy	RMS
GG	0.00	0.00	0.00	0.095
GT	2.13	2.90	2.67	0.18
TT	4.80	6.16	6.31	0.144

TABLE IX.  
Relative Energies (kcal/mol) of the Methoxymethanol Conformers, Calculated Using MP2/6-311 + G(2d, 2p) // HF/6-31G\*\*, Together with the Results of the New Force Field.

	6-311+G(2d,2p)		Charmm22	
	HF	MP2	Energy	RMS
Gg	0.00	0.00	0.00	0.100
Gg'	2.36	2.11	→Gg	
Tg	2.06	2.75	2.13	0.162
Tt	5.87	6.77	6.84	0.104

Arrows indicate transitions of conformers into others.

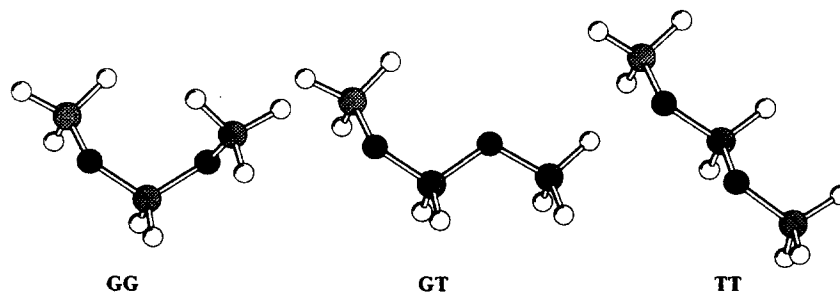
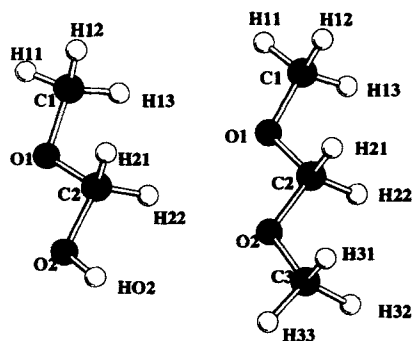


FIGURE 11. The conformers of dimethoxymethane.



**FIGURE 12.** Naming convention of the atoms in methoxymethanol (left) and dimethoxymethane (right).

**TABLE X.**  
**Assignment of Atom Types and Partial Charges to the Atoms of Dimethoxymethane.**

Atom	Atom type	Charge	Atom	Atom type	Charge
C1	CN6	-0.11	H22	HN6	0.09
H11	HN6	0.09	O2	ON6	-0.30
H12	HN6	0.09	C3	CN6	-0.11
H13	HN6	0.09	H31	HN6	0.09
O1	ON6	-0.30	H32	HN6	0.09
C2	CN6	0.10	H33	HN6	0.09
H21	HN6	0.09			

**TABLE XI.**  
**Assignment of Atom Types and Partial Charges to the Atoms of Methoxymethanol.**

Atom	Atom type	Charge	Atom	Atom type	Charge
C1	CN6	-0.04	C2	CN6	0.05
H11	HN6	0.09	H21	HN6	0.09
H12	HN6	0.09	H22	HN6	0.09
H13	HN6	0.09	O2	ON5	-0.66
O1	ON6	-0.23	HO2	HN5	0.43

**TABLE XII.**  
**Bond Parameters of the New Force Field.**

Atom 1	Atom 2	Force constant	Equilibrium distance
CN6	CN6	222.5	1.516
CN6	HN6	309.0	1.111
CN6	ON5	428.0	1.420
CN6	ON6	296.7	1.445
HN5	ON5	545.0	0.960

Force constants are given in kcal/mol/Å<sup>2</sup>, equilibrium distances in Å.

**TABLE XIII.**  
**Angle Parameters of the New Force Field.**

Atom 1	Atom 2	Atom 3	Force constant	Equilibrium angle
CN6	CN6	CN6	53.35	111.0
CN6	CN6	ON5	75.7	110.1
CN6	CN6	ON6	110.0	105.0
HN6	CN6	CN6	34.5	110.1
HN6	CN6	HN6	35.5	109.0
HN6	CN6	ON5	45.9	108.89
HN6	CN6	ON6	45.2	107.24
ON5	CN6	ON6	92.6	111.55
ON6	CN6	ON6	92.6	111.55
HN5	ON5	CN6	57.5	106.0
CN6	ON6	CN6	110.0	107.5

Force constants are given in kcal/mol/rad<sup>2</sup>, equilibrium angles in degrees.

**TABLE XIV.**  
**Torsional Parameters of the New Force Field.**

Atom 1	Atom 2	Atom 3	Atom 4	Force constant	Periodicity	Phase angle
X	CN6	CN6	X	0.15	3	0.0
ON5	CN6	CN6	ON5	0.30	3	0.0
ON5	CN6	CN6	ON5	-1.93	1	0.0
ON5	CN6	CN6	ON6	0.30	3	0.0
ON5	CN6	CN6	ON6	-2.14	1	0.0
CN6	CN6	ON6	CN6	0.15	3	0.0
CN6	CN6	ON6	CN6	0.45	1	0.0
CN6	CN6	CN6	ON5	0.68	1	0.0
CN6	CN6	CN6	ON5	0.15	3	0.0
CN6	ON6	CN6	ON5	0.20	3	0.0
CN6	ON6	CN6	ON5	-0.65	1	0.0
CN6	ON6	CN6	ON6	0.20	3	0.0
CN6	ON6	CN6	ON6	-1.35	1	0.0
X	CN6	ON6	X	0.10	3	0.0
X	CN6	ON5	X	0.140	3	0.0

Force constants are given in kcal/mol.

**TABLE XV.**  
**Nonbonded Parameters of the New Force Field.**

Atom	$E_{\min}$	$R_{\min}/2$
HN5	-0.046	0.2245
HN6	-0.022	1.3200
ON5	-0.1521	1.7000
ON6	-0.120	1.6500
CN6	-0.020	2.2750

$E_{\min}$  is given in kcal/mol,  $R_{\min}$  in Å.

## Appendix

This Appendix provides a complete listing of the HF/6-31G\*\* -derived geometries.

**TABLE A.1.**  
**Distances (Å) in the Calculated Transition States of Glycol (HF / 6-31G\*\* Geometries).**

	TS1C	TS1G	TS1O	TS2C	TS2O	TS3O	TS4O
C1-C2	1.5336	1.5504	1.5195	1.5389	1.5153	1.5107	1.5151
C1-O1	1.4021	1.3936	1.4015	1.4013	1.3957	1.4352	1.4049
C2-O2	1.4050	1.4048	1.4040	1.4039	1.4107	1.4352	1.4016
O1-H1	0.9432	0.9442	0.9428	0.9434	0.9449	0.9502	0.9404
O2-H2	0.9426	0.9419	0.9405	0.9426	0.9405	0.9502	0.9420
C1-H11	1.0860	1.0862	1.0829	1.0882	1.0900	1.0795	1.0862
C1-H12	1.0822	1.0869	1.0875	1.0833	1.0845	1.0830	1.0849
C2-H21	1.0882	1.0862	1.0863	1.0879	1.0873	1.0795	1.0888
C2-H22	1.0881	1.0869	1.0884	1.0827	1.0855	1.0830	1.0879

**TABLE A.2.**  
**Angles (Degrees) in the Calculated Transition States of Glycol (HF / 6-31G\*\* Geometries).**

	TS1C	TS1G	TS1O	TS2C	TS2O	TS3O	TS4O
O1-C1-C2	113.05	113.54	111.46	113.08	111.17	110.21	109.20
O2-C2-C1	108.49	108.65	109.36	113.14	108.52	110.21	107.41
H1-O1-C1	109.47	109.07	109.87	109.49	107.99	112.87	110.52
H1-O2-C2	109.94	110.57	110.61	110.00	111.03	112.87	110.10
H11-C1-O1	111.43	108.86	107.03	111.03	110.99	106.48	111.85
H12-C1-O1	105.75	108.86	111.80	105.52	107.29	110.55	109.64
H21-C2-O2	110.41	110.16	111.94	110.45	111.43	106.48	111.53
H22-C2-O2	111.13	110.16	109.22	106.49	108.44	110.55	111.66

**TABLE A.3.**  
**Torsional Angles (Degrees) in the Calculated Transition States of Glycol (HF / 6-31G\*\* Geometries).**

	TS1C	TS1G	TS1O	TS2C	TS2O	TS3O	TS4O
O1-C1-C2-O2	124.46	0.00	178.10	121.62	56.97	60.29	178.14
H1-O1-C1-C2	-71.27	0.00	-74.85	-68.21	-52.55	-88.11	121.11
H2-O2-C2-C1	176.33	180.00	122.11	74.65	124.17	-88.03	-177.04
H11-C1-O1-H1	50.54	121.78	165.37	53.87	69.27	110.77	0.10
H12-C1-O1-H1	167.43	-121.78	47.95	170.36	-172.98	110.05	-119.11
H21-C2-O2-H2	54.86	59.38	0.95	-50.18	2.79	110.77	63.11
H22-C2-O2-H2	-64.33	-59.38	-117.66	-166.16	-116.40	110.05	-57.52

**TABLE A.4.**  
Distances (Å) in Dimethoxymethane  
(HF/6-31G\*\* Geometries).

	gG	gT	tT
C1-O1	1.4005	1.4012	1.3935
C2-O1	1.3815	1.3678	1.3757
C2-O2	1.3815	1.3887	1.3757
C3-O2	1.4005	1.3932	1.3935
C1-H11	1.0885	1.0889	1.0891
C1-H12	1.0845	1.0831	1.0891
C1-H13	1.0814	1.0812	1.0807
C2-H21	1.0858	1.0946	1.0953
C2-H22	1.0858	1.0866	1.0953
C3-H31	1.0885	1.0893	1.0891
C3-H32	1.0845	1.0890	1.0891
C3-H33	1.0814	1.0811	1.0807

**TABLE A.5.**  
Angles (Degrees) in Dimethoxymethane  
(HF/6-31G\*\* Geometries).

	gG	gT	tT
C1-O1-C1	114.91	115.26	114.01
O1-C2-O2	113.41	110.04	106.57
C2-O2-C3	114.91	114.08	114.01
H11-C1-O1	111.02	111.00	111.64
H12-C1-O1	111.65	111.44	111.64
H13-C1-O1	107.02	106.98	107.32
H21-C2-O1	110.90	110.88	110.58
H22-C2-O1	105.91	106.90	110.58
H31-C3-O2	111.02	111.65	111.64
H32-C3-O2	111.64	111.59	111.64
H33-C3-O2	107.20	107.55	107.32
H11-C1-H12	108.70	109.01	108.53
H11-C1-H13	108.90	108.90	108.82
H31-C3-H32	108.70	108.43	108.53
H31-C3-H33	108.90	108.80	108.82
H21-C2-O2	105.91	109.43	110.57
H22-C2-O2	110.90	110.57	110.58

**TABLE A.6.**  
Torsional Angles (Degrees) in Dimethoxymethane  
(HF/6-31G\*\* Geometries).

	gG	gT	tT
C1-O1-C2-O1	66.90	65.27	179.98
O1-C2-O2-C3	66.90	-178.59	179.98
H11-C1-O1-C2	58.90	55.64	60.82
H31-C3-O2-C2	58.90	60.88	60.82

**TABLE A.7.**  
Distances (Å) in Methoxymethanol  
(HF/6-31G\*\* Geometries).

	Gg	Gg'	Tt	Tg
O2-H02	0.9444	0.9422	0.9428	0.9443
C1-O1	1.4011	1.3948	1.3932	1.3944
C2-O1	1.3808	1.3817	1.3760	1.3881
O2-C2	1.3857	1.3857	1.3811	1.3728
C1-H11	1.0884	1.0904	1.0892	1.0892
C1-H12	1.0842	1.0867	1.0892	1.0887
C1-H13	1.0814	1.0811	1.0807	1.0810
C2-H21	1.0856	1.0913	1.0940	1.0863
C2-H22	1.0843	1.0788	1.0940	1.0930

**TABLE A.8.**  
Angles (Degrees) in Methoxymethanol  
(HF/6-31G\*\* Geometries).

	Gg	Gg'	Tt	Tg
H02-O2-C2	109.06	110.93	109.74	108.90
C1-O1-C2	115.03	115.66	114.04	114.26
O1-C2-O2	112.97	113.89	106.00	109.21
H11-C1-O1	110.99	111.40	111.65	111.62
H12-C1-O1	111.59	111.78	111.64	111.53
H13-C1-O1	107.19	107.47	107.32	107.51
H21-C2-O1	111.18	109.76	110.25	110.10
H22-C2-O1	105.84	106.15	110.23	109.39
H11-C1-H12	108.74	108.94	108.52	108.49
H11-C1-H13	108.92	108.65	108.82	108.83
H21-C2-O2	105.91	110.31	111.10	106.10
H22-C2-O2	111.44	106.98	111.10	111.54

**TABLE A.9.**  
**Torsional Angles (Degrees) in Methoxymethanol (HF / 6-31G\*\* Geometries).**

	Gg	Gg'	Tt	Tg
H11-C1-O1-C2	59.42	53.58	60.50	60.25
H02-O2-C2-O1	60.89	-79.55	179.94	39.91
C1-O1-C2-O2	67.11	66.94	179.82	181.19

**TABLE A.10.**  
**Distances (Å) in Methoxyethanol (HF / 6-31G\*\* Geometries).**

	tGg'	gGg'	tTt	tTg	g'Gt	g'Gg	gTt	gTg'	gTg	tGt	tGg	gGt	TS
O1-C1	1.3962	1.3966	1.4019	1.4013	1.4037	1.4035	1.4018	1.4017	1.4018	1.3997	1.3970	1.3984	1.3956
C1-C2	1.5136	1.5181	1.5133	1.5180	1.5135	1.5203	1.5191	1.5235	1.5235	1.5101	1.5153	1.5171	1.5445
C2-O2	1.3990	1.4045	1.3946	1.3931	1.3950	1.3934	1.3982	1.3972	1.3975	1.3928	1.3990	1.3943	1.3878
O2-C3	1.3940	1.3967	1.3925	1.3928	1.3995	1.3990	1.3948	1.3956	1.3947	1.3914	1.3919	1.3923	1.3903
O1-HO1	0.9445	0.9448	0.9420	0.9427	0.9424	0.9431	0.9421	0.9429	0.9428	0.9420	0.9430	0.9422	0.9424
C1-H11	1.0887	1.0899	1.0876	1.0820	1.0878	1.0825	1.0878	1.0876	1.0821	1.0875	1.0823	1.0888	1.0889
C1-H12	1.0839	1.0844	1.0876	1.0873	1.0904	1.0904	1.0887	1.0828	1.0883	1.0902	1.0907	1.0908	1.0889
C2-H21	1.0894	1.0834	1.0892	1.0893	1.0889	1.0929	1.0831	1.0861	1.0831	1.0893	1.0939	1.0830	1.0906
C2-H22	1.0906	1.0890	1.0892	1.0928	1.0854	1.0855	1.0879	1.0883	1.0914	1.0092	1.0921	1.0913	1.0906
C3-H31	1.0885	1.0881	1.0890	1.0888	1.0828	1.0829	1.0820	1.0819	1.0818	1.0889	1.0894	1.0898	1.0899
C3-H32	1.0887	1.0876	1.0890	1.0892	1.0890	1.0898	1.0884	1.0884	1.0888	1.0900	1.0896	1.0877	1.0899
C3-H33	1.0818	1.0818	1.0820	1.0818	1.0825	1.0822	1.0880	1.0819	1.0880	1.0819	1.0816	1.0818	1.0817
O2..HO1	2.3742	2.3755	4.2679	3.9216	3.7815	3.4836	4.3225	3.9395	3.9595	3.6336	3.2103	3.7330	

**TABLE A.11.**  
**Angles (Degrees) in Methoxyethanol (HF / 6-31G\*\* Geometries).**

	tGg'	gGg'	tTt	tTg	g'Gt	g'Gg	gTt	gTg'	gTg	tGt	tGg	gGt	TS
O1-C1-C2	111.46	111.02	107.23	111.31	109.61	114.05	107.00	111.06	111.12	108.49	113.67	108.78	110.95
HO1-O1-C1	107.89	108.07	109.98	109.89	109.96	109.79	110.14	109.87	110.00	109.69	109.98	109.99	108.82
C1-C2-O2	107.33	110.90	107.79	107.97	113.61	114.24	111.48	111.96	111.85	109.33	109.65	114.35	111.33
C2-O2-C3	114.69	115.73	114.34	114.53	116.51	116.75	115.71	115.71	115.86	114.23	114.38	116.07	113.60
H11-C1-C2	109.12	110.35	109.23	109.40	108.74	108.96	109.00	109.31	109.13	108.71	109.07	110.58	108.89
H12-C1-C2	109.74	109.68	109.24	109.52	108.55	108.70	110.39	110.63	110.81	108.71	108.45	107.87	108.89
H21-C2-C1	109.86	109.15	109.58	109.57	109.26	109.83	108.88	109.28	108.79	109.11	109.96	108.36	109.40
H22-C1-C2	110.43	110.83	109.58	110.06	108.12	108.23	109.59	109.59	110.15	109.20	108.95	108.79	109.41
H31-C3-O2	111.42	111.11	111.49	111.48	112.04	112.08	107.38	107.34	107.38	111.52	111.55	111.47	111.67
H32-C3-O2	111.37	112.35	111.49	111.48	111.06	111.05	111.32	111.31	111.29	111.63	111.60	112.52	111.67
H33-C3-O2	107.70	107.37	107.68	107.67	106.92	106.96	112.37	112.37	114.41	107.65	107.62	107.29	107.54
H11-C1-O1	111.12	110.86	111.58	107.10	111.15	106.46	111.64	111.77	106.99	111.46	106.41	111.12	110.52
H12-C1-O1	107.30	107.43	111.58	111.77	110.58	110.63	111.09	106.48	111.21	110.83	111.16	111.16	110.52
H21-C2-O2	110.28	106.49	111.09	111.22	111.11	110.66	107.57	106.91	107.55	110.87	110.48	106.39	109.95
H22-C2-O2	110.67	110.93	111.09	110.62	106.53	106.20	111.44	111.46	110.86	110.36	110.73	110.57	109.95
H31-C3-H32	108.53	108.52	108.41	108.43	108.69	108.76	108.77	108.81	108.75	108.39	108.35	108.44	108.27
H31-C3-H33	108.93	108.81	108.84	108.88	109.49	109.41	108.51	108.47	108.47	108.82	108.81	108.71	108.27

**TABLE A.12.**  
**Torsional Angles (Degrees) in Methoxyethanol (HF / 6-31G\*\* Geometries).**

	tGg'	gGg'	tTt	tTg	g'Gt	g'Gg	gTt	gTg'	gTg	tGt	tGg	gGt	TS
HO1-O1 -C1-C2	-53.76	-47.46	180.00	74.84	-173.32	68.93	-176.74	-72.85	72.96	-167.14	59.62	-175.85	-179.99
O1-C1- C2-O2	60.63	57.91	61.80	179.85	73.16	72.04	179.43	178.89	177.36	72.16	62.28	64.57	0.00
C3-O2- C2-C1	-175.82	88.76	180.00	-178.48	-87.36	-80.07	60.26	88.04	89.07	-174.88	-178.87	77.96	180.00
H31-C3 -O2-C2	60.44	60.99	60.66	60.54	67.75	68.32	180.03	179.39	180.16	61.09	60.90	55.52	60.67

**TABLE A.13a.**  
**Distances (Å) in Glycerol (HF / 6-31G\*\* Geometries).**

	1	2	3	4	5	6	7	8	9
C1-C2	1.5276	1.5293	1.5186	1.5221	1.5236	1.5167	1.5200	1.5190	1.5241
C1-O1	1.4017	1.4006	1.4080	1.4087	1.3966	1.4056	1.4075	1.3966	1.4076
O1-H1	0.9463	0.9457	0.9422	0.9434	0.9450	0.9422	0.9422	0.9442	0.9435
C2-C3	1.5231	1.5224	1.5192	1.5198	1.5186	1.5180	1.5290	1.5216	1.5282
C2-O2	1.4052	1.3948	1.4037	1.4032	1.4066	1.4043	1.4046	1.4184	1.4036
O2-H2	0.9456	0.9456	0.9450	0.9454	0.9461	0.9445	0.9427	0.9429	0.9428
C1-H11	1.0882	1.0890	1.0850	1.0805	1.0883	1.0881	1.0860	1.0862	1.0857
C1-H12	1.0834	1.0826	1.0881	1.0875	1.0847	1.0885	1.0876	1.0836	1.0828
C2-H21	1.0879	1.0871	1.0900	1.0932	1.0849	1.0887	1.0884	1.0881	1.0912
C3-O3	1.4073	1.4106	1.3975	1.3964	1.4070	1.3947	1.3939	1.3960	1.3951
C3-H31	1.0866	1.0856	1.0877	1.0878	1.0869	1.0842	1.0902	1.0910	1.0897
C3-H32	1.0842	1.0893	1.0843	1.0845	1.0883	1.0897	1.0855	1.0843	1.0856
O3-H3	0.9446	0.9422	0.9451	0.9451	0.9422	0.9449	0.9450	0.9449	0.9449
O1..H2	2.2066	2.2482	2.2425	2.2513	3.2818	2.3309	4.2847	3.4498	4.3386
O1..H3	3.1061	3.6663	4.1905	4.1896	5.1317	4.7327	2.0905	4.2252	2.1535
O2..H1	2.9860	3.0120	3.5241	3.2219	2.3242	3.5557	4.2499	2.3630	3.9436
O2..H3	2.5526	3.7126	2.3480	2.3555	3.5601	2.3128	3.8975	2.3697	3.9099
O3..H1	2.1905	2.0826	4.7445	4.8070	4.2450	5.5711	3.6650	4.3348	3.1541
O3..H2	2.9656	2.8290	3.5583	3.5108	2.2610	3.6216	3.8574	3.3338	3.8714



**TABLE A.13b.**  
**Distances (Å) in Glycerol (HF / 6-31G\*\* Geometries) (Continued).**

	10	11	12	13	14	15	16
C1-C2	1.5198	1.5236	1.5282	1.5247	1.5282	1.5251	1.5196
C1-O1	1.4070	1.3937	1.4060	1.4064	1.4070	1.3925	1.3946
O1-H1	0.9434	0.9455	0.9437	0.9423	0.9437	0.9444	0.9447
C2-C3	1.5179	1.5224	1.5251	1.5287	1.5280	1.5254	1.5196
C2-O2	1.4034	1.4061	1.4044	1.4045	1.4040	1.4096	1.4175
O2-H2	0.9449	0.9464	0.9426	0.9443	0.9444	0.9432	0.9459
C1-H11	1.0831	1.0918	1.0897	1.0861	1.0861	1.0914	1.0931
C1-H12	1.0879	1.0852	1.0828	1.0911	1.0858	1.0828	1.0838
C2-H21	1.0921	1.0854	1.0910	1.0830	1.0854	1.0907	1.0833
C3-O3	1.3948	1.4086	1.3962	1.3924	1.3940	1.4019	1.3946
C3-H31	1.0843	1.0822	1.0895	1.0945	1.0940	1.0904	1.0838
C3-H32	1.0895	1.0875	1.0820	1.0830	1.0827	1.0840	1.0931
O3-H3	0.9449	0.9423	0.9444	0.9449	0.9448	0.9463	0.9447
O1..H2	2.3269	3.3168	3.9536	3.8981	3.9254	3.7926	3.1267
O1..H3	4.8029	4.2817	2.1715	2.0661	2.1342	2.8852	4.7827
O2..H1	3.2654	2.2952	3.9637	4.3110	3.9656	3.0665	2.3560
O2..H3	2.3264	3.3375	3.8885	3.8991	3.9134	2.3672	2.3546
O3..H1	5.0674	4.3170	3.0984	3.6657	3.1310	2.1404	4.7833
O3..H2	3.6558	2.2706	4.3191	3.8964	3.9022	3.2741	3.1251

**TABLE 14a.**  
**Angles (Degrees) in Glycerol (HF / 6-31G\*\* Geometries).**

	1	2	3	4	5	6	7	8	9
O1-C1-C2	111.48	111.65	106.64	110.37	110.52	106.65	108.70	111.10	112.54
H1-O1-C1	108.51	108.50	110.36	110.03	107.79	110.45	110.27	107.89	109.88
C1-C2-C3	113.26	113.23	112.80	112.99	113.49	113.09	113.15	113.51	113.05
C1-C2-O2	109.99	110.12	110.03	109.79	109.49	110.19	104.68	106.11	104.96
H2-O2-C2	108.16	107.89	108.27	108.43	107.49	108.60	110.06	110.42	110.30
H11-C1-C2	110.16	110.27	109.52	109.65	109.66	109.60	109.17	109.41	109.34
H12-C1-C2	109.39	108.92	109.98	110.55	110.29	110.25	108.55	109.62	109.00
H21-C2-C1	108.40	108.42	108.40	108.93	108.28	108.54	108.97	108.36	109.18
O3-C3-C2	111.72	109.38	111.73	111.62	107.40	111.13	112.93	111.84	112.87
H31-C3-C2	109.21	108.44	108.53	108.63	108.98	110.26	109.31	109.04	109.09
H32-C3-C2	110.56	109.58	110.34	110.31	110.28	109.14	108.58	110.32	108.88
H3-O3-C3	107.94	110.49	107.62	107.67	110.54	107.89	108.49	108.14	108.42
H11-C1-O1	111.57	111.52	111.09	106.65	111.23	110.78	111.14	111.46	111.29
H12-C1-O1	106.25	106.33	110.97	111.26	107.21	111.00	111.04	107.20	106.82
H21-C2-O2	108.17	106.96	110.17	109.95	106.28	109.89	111.24	109.92	110.95
H32-C3-O3	110.42	110.65	111.00	111.06	110.63	107.17	111.95	110.84	111.90
H33-C3-O3	106.85	110.22	107.28	107.31	111.14	110.99	106.72	107.34	106.68

**TABLE A.14b.**  
**Angles (Degrees) in Glycerol (HF/6-31G\*\* Geometries) (Continued).**

	10	11	12	13	14	15	16
O1-C1-C2	110.39	110.91	113.23	109.27	113.19	114.76	111.32
H1-O1-C1	109.92	107.72	110.04	110.53	109.84	109.42	108.56
C1-C2-C3	113.25	113.82	113.22	113.72	113.66	113.89	113.96
C1-C2-O2	109.98	109.13	108.94	108.51	108.93	108.40	109.85
H2-O2-C2	108.80	108.07	110.61	110.13	110.14	110.06	109.69
H11-C1-C2	109.79	109.66	109.70	108.88	109.12	107.86	109.56
H12-C1-C2	110.80	110.44	108.92	109.04	109.45	108.28	110.28
H21-C2-C1	109.07	108.12	109.58	109.05	109.32	106.80	108.95
O3-C3-C2	111.22	111.10	112.67	113.49	113.34	111.64	111.33
H31-C3-C2	110.27	109.02	109.10	109.28	109.18	109.34	110.29
H32-C3-C2	109.02	110.82	108.24	107.86	108.19	110.72	109.56
H3-O3-C3	108.00	110.66	108.83	108.90	108.82	107.86	108.54
H11-C1-O1	106.28	110.63	110.69	111.22	111.27	111.27	110.90
H12-C1-O1	111.22	107.34	106.68	110.47	106.10	106.73	107.31
H21-C2-O2	109.70	106.53	110.93	106.43	106.01	110.49	104.86
H32-C3-O3	107.10	106.35	111.77	111.33	111.27	110.39	107.32
H33-C3-O3	111.08	111.39	107.31	107.22	107.26	107.19	110.89

**TABLE A.15a.**  
**Torsional Angles (Degrees) in Glycerol (HF/6-31G\*\* Geometries).**

	1	2	3	4	5	6	7	8	9
H1-O1-C1-C2	-61.15	-61.95	-169.53	77.64	-48.03	-171.36	178.51	-57.20	-76.39
O1-C1-C2-C3	73.09	75.02	174.92	172.23	179.64	177.62	-55.68	-179.97	-57.80
O1-C1-C2-O2	-49.07	-50.08	56.22	53.29	56.72	58.85	-176.29	59.95	-178.47
H2-O2-C2-C1	19.65	39.43	-45.91	-38.35	80.81	-54.47	-167.84	-154.23	-171.14
O2-C2-C3-O3	60.54	71.26	58.71	59.15	56.71	-58.89	-166.65	56.55	-171.12
H3-O3-C3-C2	-68.95	-170.45	-54.48	-54.54	-171.55	51.49	-54.69	-49.85	-59.71

**TABLE A.15b.**  
**Torsional Angles (Degrees) in Glycerol (HF/6-31G\*\* Geometries) (Continued).**

	10	11	12	13	14	15	16
H1-O1-C1-C2	78.15	-45.87	-70.16	-177.46	-74.56	-51.34	-43.61
O1-C1-C2-C3	175.10	178.54	-59.42	-55.45	-57.29	61.86	-178.15
O1-C1-C2-O2	56.13	55.23	-177.64	-179.23	178.89	-59.72	58.09
H2-O2-C2-C1	-46.01	86.10	-72.02	71.86	69.02	-158.03	63.07
O2-C2-C3-O3	-58.71	53.06	-171.09	-165.09	-169.40	57.20	-58.00
H3-O3-C3-C2	52.81	86.67	-60.63	-52.00	-57.24	-49.81	43.56

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